

# ATRP OF VINYL ACETATE CATALYZED BY RUTHENIUM (II) COMPLEX

Olvera-Mancilla J <sup>1</sup>, Diaz-Camacho F <sup>1</sup>, Ronan Le Lagadec <sup>2</sup>, Alexandrova L <sup>1\*</sup>.

<sup>1</sup>Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior S/N, Ciudad Universitaria, Coyoacán, 04511 México Distrito Federal, México.

<sup>2</sup>Instituto de Química, Universidad Nacional Autónoma de México, Circuito exterior S/N, Ciudad Universitaria, Coyoacán, 04511 México Distrito Federal, México.

<sup>1\*</sup> To whom correspondence address. [olverajessica@hotmail.com](mailto:olverajessica@hotmail.com)

**Abstract:** Both  $[\text{Ru}(\text{Phpy})(\text{NCMe})_4]^+\text{PF}_6^-$  and  $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{dmmba})(\text{NCMe})]^+\text{PF}_6^-$  were used to induce Atom Transfer Radical Polymerization of vinyl acetate (VOAc) in bulk,  $\text{CCl}_4$  was used as initiator and  $\text{Al}(\text{Oi-Pr})_3$  as additive. Two reactions temperatures were tested 65° and 80° C. For both reaction systems higher conversions were obtained when reaction temperature increased and good agreement between experimental and theoretical molecular weights. When  $[\text{Ru}(\text{Phpy})(\text{NCMe})_4]^+\text{PF}_6^-$  **a** catalyst was used molecular weights of 12,000 were obtained at 7 % conversion and they were not changed further while PDIs remained less than 1.5 at 80° C. In contrast, the polymerizations induced by the complex  $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{dmmba})(\text{NCMe})]^+\text{PF}_6^-$  **b** demonstrated much better control POVAc with living radical behavior ( $M_n$  increased linearly with conversion), low  $M_w/M_n$  was gotten in the system.

## Introduction.

Atom transfer radical polymerization (ATRP) is one of the most versatile controlled radical polymerization techniques. Indeed, it allows polymerizing a wide variety of monomers, while offering a well-defined polymer with controlled molecular weight and low polydispersity. The importance of controlling VOAc polymerization arises not only from its industrial importance but also from the fact that the control of VOAc polymerization has been considered highly difficult.

Vinyl acetate (VOAc) is one of the most challenging monomer to polymerize by living radical mechanism. Unlike traditionally used for ATRP monomers, such as (meth)acrylates and styrene, VOAc lacks a conjugating substituent, and thus its propagating radical is highly reactive and tends to undergo easily chain transfer or termination reactions. To our knowledge only a few relatively successful controlled polymerizations of VOAc have been achieved till the moment [1, 2].

Here we report polymerization of VOAc catalyzed by two cyclometalated Ru(II) compounds  $[\text{Ru}(\text{Phpy})(\text{NCMe})_4]^+\text{PF}_6^-$  (**a**) and  $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{dmmba})(\text{NCMe})]^+\text{PF}_6^-$  (**b**) [3], where Phpy and dmmba are phenylpyridine and N,N-dimethylbenzylamine respectively. These ruthenacycles had been tested before for styrene (St) and methyl methacrylate (MMA) polymerizations. Polymerizations of both mentioned monomers induced by these complexes were fast and poorly controlled: molecular weights were high from the very beginning and almost did not depend on conversions and polydispersity indexes (PDIs) were broad (between 1.7 and 2) [4].

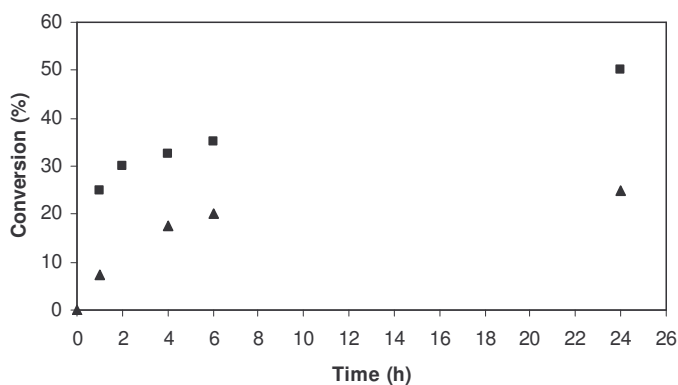
However the same complexes applied for VOAc polymerization demonstrated quite different behavior and acceptable level of control has been achieved using one of them,  $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{dmba})(\text{NCMe})]^+\text{PF}_6^-$ .

## Experimental.

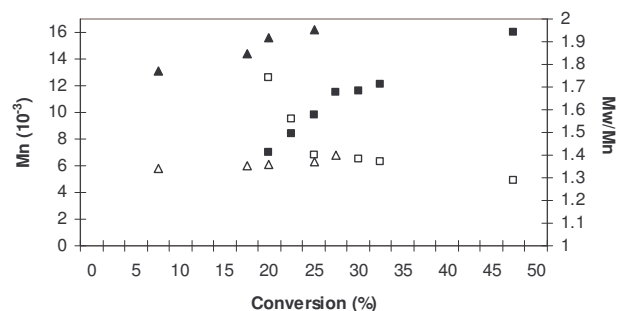
The vinyl acetate was washed with NaOH, dried over  $\text{MgSO}_4$  anhydrous and distilled. The catalysts were prepared as described in the reference [3]. The others reagents were used as received from Aldrich Chem Co.  $\text{CCl}_4$  was used as initiator in both cases. Molecular weight measurements were performed using Waters 2695 equipment with refractive index detector. The ratio  $[\text{VOAc}]_0:[\text{Ru(II)}]_0:[\text{CCl}_4]_0:[\text{Al(Oi-Pr)}]_0$  was set at 200:1:1:1 for all the experiments.

## Results and Discussion.

Polymerizations were rather slow with both of the catalysts: about 25 and 50 % conversions were reached in 24 h with  $[\text{Ru}(\text{Phpy})(\text{NCMe})_4]^+\text{PF}_6^-$  (**a**) and  $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{dmba})(\text{NCMe})]^+\text{PF}_6^-$  (**b**) respectively. However in case of the complex **a** molecular weights of 12,000 were obtained at 7 % conversion and they were not changed further while PDIs remained less than 1.5 (see Fig 1 and 2). The polymerizations induced by the complex **b** demonstrated much better control: molecular weights depended linearly on conversions and PDIs were also getting lower with conversions.



**Figure 1.** Polymerization of VOAc promote by  $[\text{Ru}(\text{C}_6\text{H}_4\text{-2-C}_5\text{H}_4\text{N})(\text{CH}_3\text{CN})_4]^+\text{PF}_6^-$  (**a**) and  $[\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)(\text{CH}_3\text{CN})]^+\text{PF}_6^-$  using  $\text{CCl}_4$  as initiator and  $\text{Al(Oi-Pr)}_3$  as additive. Conditions: 80 °C  $[\text{VOAc}]/[\text{Ru(II)}]_0/[\text{CCl}_4]_0/[\text{Ali.OPr}]_0 = 200/1/1/1$ . (▲-complex a, ■-complex b).



**Figure 2.** Dependence of molecular weight ( $M_{n,SEC}$ ) and polydispersity ( $M_w/M_n$ ) on monomer conversion. ( $\blacktriangle$  Mn-complex a,  $\blacksquare$  Mn-complex b;  $\triangle$   $M_w/M_n$ -complex a,  $\square$   $M_w/M_n$ -complex b).

As shown in figure 2 the number-average molecular weights increased linearly with the conversion and were quite close to the calculated values with complex **b**; while in the case of complex **a** molecular weights jumped abruptly from the very beginning. The size-exclusion chromatography (SEC) curves of the polymer synthesized with both complexes **a** and **b** were unimodal and gave relatively narrow polydispersities ( $M_w/M_n < 1.5$ ).

## Conclusions.

In summary, polymerizations of VOAc using  $CCl_4$  as initiator in the presence of  $[Ru(Phpy)(NCMe)_4]^+PF_6^-$  **a** and  $[Ru(\eta^6-C_6H_6)(C_6H_4-2-CH_2NMe_2)(CH_3CN)]^+PF_6^-$  **b** provided polymers with high yields and  $M_w/M_n < 1.5$ .

The syntheses of pVOAc induced by the complex **b** demonstrated better control over molecular weights ( $M_{n, SEC} = 16000$ ) and the polymerization was faster than those obtained with **a**. Number average molecular weights were only slightly higher than predicted by theory. The PDI was also getting lower with conversions and the  $M_n$  depended linearly on conversions.

## Acknowledgments.

We are thankful to M.C. S. Lopez for GPC analysis and CONACyT (Grand D 40135Q) for financial support.

## References.

1. Masayuki Wakioka, Kyung-Youl Baek, Tsuyoshi Ando, Masami Kamigaito, and Mitsuo Sawamoto. *Macromolecules*. 2002, 35, 330-333.
2. Jianhui Xia, Hyung-jong Paik, and Krzysztof Matyjaszewski. *Macromolecules*. 1999, 32, 8310-8314.
3. Susana Fernandez, Michel Pfeffer, Vincent Ritleng, and Claude Sirlin. *Organometallics*. 1999, 18, 2390
4. L. Alexandrova, F D Camacho, G. V. López, and R. L. Lagadec. PPLYCHAR. Conference Proceedings, Japan, 2006.





